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# Inorganic constituents in surface runoff from urbanised areas in winter: the case study of the city of Brest, Belarus

**KEYWORDS**
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**Abstract**

The aim of this paper was to study the inorganic constituents of snow and snowmelt surface runoff in a case study of the city of Brest and to indicate components that could pose a threat to the environment. Samples of snow and snowmelt runoff were analysed for the following parameters: total suspended solids, pH, the contents of nitrate, phosphate and ammonium ions, and of heavy metals. The concentrations of most of these pollutants were higher in the snowmelt runoff than in snow. The concentrations of pollutants in the snowmelt surface runoff exceeded the levels established by national regulations (maximum permissible concentrations).

## 1. Introduction

Urban environments are characterised by a significant percentage of impervious surfaces (such as roads, pavements and roofs), a reduced area of natural sinks and a large number of pollution sources (Parikh 2005). The impervious surfaces alter the natural hydrology because they do not permit rain and snowmelt to infiltrate into the soil as at natural sites; this water thus contributes a significant proportion to the surface runoff.

Urban surface runoff can carry a considerable amount of impurities, sometimes comparable to that of municipal wastewaters (Chouli 2007). Storm runoff discharges from urban areas can give rise to various adverse effects in receiving water quality: deposition of contaminated sediments (Marsalek 2005), increased toxicity due to pollutants from traffic (Roger 1998, Han 2006) and nutrient pollution and eutrophication (Marsalek 2003, Bartlett et al. 2012). Although surface rainwater runoff has frequently been investigated in many countries, little attention has been paid to urban snowmelt runoff (Buttle 1988). In countries with a moderate continental climate, winter surface runoff quality is influenced primarily by litter and rubbish from streets, soil and pavement erosion, emissions from vehicles and industry, road de-icing composites, street cleaning, salting and snow removal etc., as well as the weather conditions (Sujkova et al. 2012, Shhukin et al. 2012). Up to 60% of the annual pollutant load related to surface runoff originates from the winter period, because pollutants are accumulated in the snowpack and then released during intermittent and final snowmelt (Marsalek 2003).

In cities where the surface runoff drainage system was designed in the mid-20th century, the common practice has been to discharge the runoff directly into watercourses, since for a long time urban surface runoff was not considered harmful to the environment. In the city of Brest, the surface runoff from the majority of drainage collectors is discharged directly into the River Mukhavets. The Mukhavets is the main river of Brest Polesye, a watercourse important for the socio-economic development of the region. Four towns are situated on the banks of the Mukhavets, and the river provides a water supply, shipping, fishing and recreation for their populations. The river is also the main recipient of wastewaters (Volchek et al. 2005). Furthermore, the Mukhavets is a tributary of the transboundary Western Bug, a river belonging to the Baltic Sea catchment area. This means that the contaminants entering the Mukhavets contribute to the total amount of pollutants carried to the Baltic Sea by river systems.

The aim of this paper was to study the inorganic constituents of snow and snowmelt runoff in urban areas as exemplified by the city of Brest, and to indicate the components that could pose a potential environmental threat. Accordingly, the concentrations of inorganic ions such as chloride, phosphate, nitrate and ammonium, heavy metals (HM) – Pb, Cu, Mn, Zn, Fe, Ni, Cr – as well as total suspended solids (TSS) and pH were determined in samples of snow and snowmelt runoff collected from December 2012 to April 2013.

To evaluate the impact on surface waters, all the results were compared with the national regulations for surface waters – the maximum permissible concentrations (MPC) for fish breeding waters (Regulation No. 43/42). TSS concentrations were compared with the national regulation for urban surface runoff discharges (TCGP, 2012 – Technical Code 17.06-08-2012 (02120)), because the regulation for fish breeding waters does not limit the concentration of TSS, but only states its maximum permissible increase after wastewater discharges.

## 2. Material and methods

### 2.1. Sampling

Three sampling sites typical of urban areas were chosen in the city of Brest for the assessment of inorganic pollutants in snow and snowmelt runoff (Figure 1). Sampling site 1 was a street in the city centre with heavy traffic, and a large number of public transport and public institutions. Sampling site 2 was an area with mainly residential development and no public transport. Sampling site 3 was an area with a road junction and a large car park in front of a supermarket, with less intense public transport than at site 1 and mainly residential development. The drainage system at each site has one large central collector, which carries storm and snowmelt surface runoff directly to the River Mukhavets.

The sample collection period was from December 2012 to April 2013. The snow samples were collected during every fall of snow that was heavy


**Figure 1.** General scheme of the sample sites (black lines represent central drainage collectors, asterisks snow sample points)

enough to yield a sufficient amount of snow for analysis. The sampling vessels for snow (plastic, total volume 1.5 L for each sample) were placed in a green area of each site for 12 hours during snow falls to prevent any accidental contamination of the samples (e.g. by traffic, litter or pets). After the samples of snow had been taken to the laboratory, they were melted at room temperature and analysed within 24 hours.

Winter in Belarus is characterised by successive periods of cold and warm weather. During the sampling period, thaws warm enough to produce runoff (including the final snow melt in April) occurred several times, and each time the runoff was sampled and analysed. The snowmelt surface runoff was sampled at the ends of the drainage pipes that carry effluent from the target sites to the River Mukhavets; the samples were collected in clean plastic vessels (1 L volume for each sample) and analysed within 24 hours. Four snow samples and six runoff samples were taken from each site.

### 2.2. Analysis

The contaminants were analysed by standard methods (Standard Methods 1992, Aleshka 1997). Each parameter was analysed in two parallel measurements.

TSS were measured gravimetrically. Paper filters (pore size 2–3 $\mu$m) were weighed in weighing bottles. Then 100 mL of a sample (or a smaller volume diluted to 100 mL) was passed through the filter, the filter in the same weighing bottle was dried at 110°C, cooled to room temperature and weighed again until constant weight. The content of TSS was calculated as the difference between the two weights.

The concentration of chloride ions was measured by titration against silver nitrate and potassium chromate as indicator.

The concentrations of nitrate, phosphate and ammonium ions were measured photometrically on an MS-122 PROSCAN Special Instruments (2010) spectrophotometer (Department of Chemistry, A. S. Pushkin Brest State University). The determination of phosphate ions was based on the reaction of phosphate ions with partly reduced hexavalent molybdenum resulting in the formation of a blue-coloured complex. The determination of ammonium ions was based on their ability to form a yellow-brownish compound with Nessler's reagent. Nitrate ions were determined on the basis of their reaction with sodium salicylate in the presence of sulphuric acid; this yields a mixture of salts of 3-nitrosalicylic and 5-nitrosalicylic acids which is coloured yellow in an alkaline medium.

Heavy metals (Pb, Cu, Mn, Zn, Fe, Ni, Cr) were measured by atomic absorption spectrometry on a SOLAAR Mkll M6 Double Beam (2004) spectrometer with flame atomiser (Laboratory of Biochemistry, Poleski Agrarian-Ecological Institute NAS of Belarus).

The total relative analytical errors were as follows: pH 0.2; TSS 10%; phosphate 7.85%; nitrate 9.74%; ammonium 8.73%; chloride 5%; HM $\leq$ 5%.

## 3. Results and discussion

The results of the snow analysis are presented in Table 1. The pH of all the samples was slightly acidic (overall mean value 6.57). Zn and $PO_4^{3-}$ concentrations exceeded MPCs in all the samples.

The results of the snowmelt runoff analysis are presented in Table 2. The concentrations of TSS, $Cl^-$, $PO_4^{3-}$, $NH_4^+$, Mn and Zn exceeded MPC in the samples from all the sites. The overall mean concentrations of Cu and Ni also exceeded MPC, and the pH was slightly alkaline (see Table 2).

According to the initial results, several components can have a potential environmental impact.

All the pollutants tested for were found in the samples of snow. The contaminants in the atmospheric precipitation in Belarus are mainly of trans-boundary origin, although contamination by reduced nitrogen is basically of local origin (Struk 2002).

The pH values do not deviate from MPCs (except snow at site 2) and change from slightly acidic in precipitation to slightly alkaline in the snowmelt runoff (see Figure 2a); this is the result of contact with concrete

**Table 1.** Physical and chemical parameters measured in the snow samples

| Parameter | Mean concentrations [mg L$^{-1}$]* | | | Overall mean | MPC |
|---|---|---|---|---|---|
| | Site 1 | Site 2 | Site 3 | [mg L$^{-1}$] | [mg L$^{-1}$] |
| pH | 6.67 | **6.30**** | 6.80 | 6.57 | 6.5–8.5 |
| TSS | 0 | 0 | 0 | 0 | 20 |
| $Cl^-$ | 1.930 | 4.610 | 0 | 2.610 | 300 |
| $NO_3^-$ | 0.390 | 0.480 | 0.100 | 0.370 | 40 |
| $PO_4^{3-}$ | **1.070**** | **1.260**** | **1.800**** | **1.370**** | 0.202 |
| $NH_4^+$ | 0.200 | 0.310 | 0.270 | 0.260 | 0.474 |
| Pb | 0.007 | 0.012 | 0.013 | 0.011 | 0.100 |
| Cu | 0.002 | **0.006** | 0.002 | 0.004 | 0.004 |
| Mn | 0.003 | 0.005 | 0.007 | 0.005 | 0.050 |
| Zn | **0.256**** | **0.686**** | **0.401**** | **0.481**** | 0.016 |
| Fe | 0.112 | 0.120 | 0.098 | 0.112 | 0.340 |
| Ni | 0.001 | 0.006 | 0.005 | 0.005 | 0.010 |
| Cr | **0.006**** | 0 | 0 | 0.002 | 0.005 |

*The unit does not apply to pH.
**Values that exceeded the maximum permissible concentrations (MPC).

**Table 2.** Physical and chemical parameters measured in the snowmelt runoff samples

| Parameter | Mean concentrations [mg $L^{-1}$]* | | | Overall mean [mg $L^{-1}$] | MPC [mg $L^{-1}$] |
|---|---|---|---|---|---|
| | Site 1 | Site 2 | Site 3 | | |
| pH | 7.90 | 7.68 | 7.57 | 7.73 | 6.5–8.5 |
| TSS | **2860**** | **348**** | **140**** | **1266**** | 20 |
| $Cl^-$ | **4380**** | **2742**** | **504**** | **2881**** | 300 |
| $NO_3^-$ | 1.580 | 2.890 | 1.260 | 2.070 | 40 |
| $PO_4^{3-}$ | **2.020**** | **3.250**** | **2.780**** | **2.680**** | 0.202 |
| $NH_4^+$ | **1.140**** | **1.070**** | **1.090**** | **1.100**** | 0.474 |
| Pb | 0.017 | 0.015 | 0.017 | 0.016 | 0.100 |
| Cu | **0.035**** | 0.003 | **0.007**** | **0.016**** | 0.004 |
| Mn | **0.183**** | **0.146**** | **0.116**** | **0.153**** | 0.050 |
| Zn | **0.626**** | **0.323**** | **0.617**** | **0.508**** | 0.016 |
| Fe | 0.192 | **0.492**** | 0.139 | 0.295 | 0.340 |
| Ni | **0.011**** | 0.008 | **0.012**** | 0.010 | 0.010 |
| Cr | **0.020**** | 0 | 0 | **0.008**** | 0.005 |

*The unit does not apply to pH.
**Values that exceeded the maximum permissible concentrations (MPC).

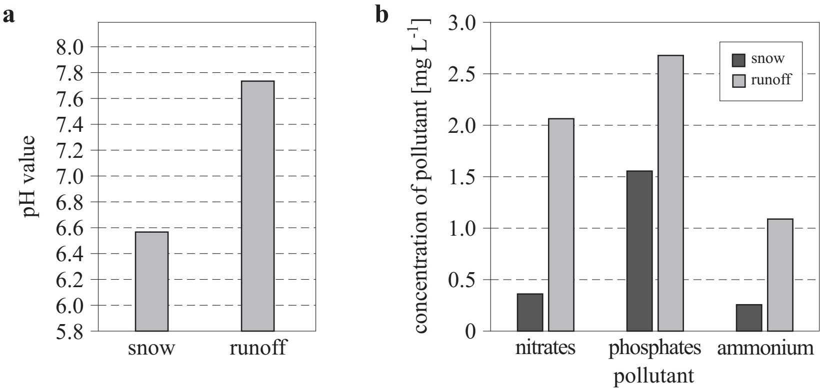


**Figure 2.** Overall mean pH values (a) and overall mean concentrations of nitrate, phosphate and ammonium ions (b) in snow and snowmelt runoff

pavement covers, buildings and road constructions, and the solubilisation and accumulation of alkaline components.

TSS and chloride ions are the main pollutants in the snowmelt runoff. The average concentrations of TSS and chloride are several times higher than MPCs, their overall mean concentrations exceeding MPCs 63.3 and 9.6 times respectively. This is due to the de-icing of streets and roadways, which is done using composites containing a mixture of sand and sodium chloride. The TSS and chloride concentrations most probably depend on the

**Figure 3.** Retained solids on roads and pavements after snow melting, Brest, Belarus (February 2013)

frequency of street cleaning and de-icing and snow removal. The highest TSS and chloride concentrations in the snowmelt runoff samples were obtained for sampling site 1, which has the heaviest traffic and public transport and the most intensive salting and snow removal, because all the applied reagents are readily washed away by the snowmelt under such conditions.

A substantial percentage of TSS (with coarser particles) remains on the roads and pavements during snow melting periods (see Figure 3). These solids present a potential contamination threat for the river waters, as they can be washed into the receiving waters by surface runoff from a later portion of snowmelt (Westerlund et al. 2006) or during later storm events. Moreover, suspended solids can adsorb pollutants on their surface and then release them on entering the receiving waters, causing long-term pollution effects. The elevated TSS levels alter natural sedimentation processes in watercourses and can result in increased turbidity, depletion of dissolved oxygen, inhibition of benthic aerobic microorganisms and impairment of photosynthesis (Marsalek et al. 2005, Sujkova et al. 2012).

Chloride ions are natural components of surface waters, but the continuous discharge of wastes with high chloride ion concentrations can increase the total water salinity. Both aquatic and terrestrial ecosystems can be affected by exposure to high chloride ion concentrations (Perera et al. 2013). Secondary salinisation of rivers is a growing threat (Cañedo-Argüelles et al. 2013): elevated chloride levels render surface waters unsuitable as an environment for many freshwater limnetic organisms and as a potable water supply. Moreover, chloride ions can alter the equilibrium between adsorbed and dissolved metals in snowmelt (Bäckström et al. 2004), thus leading to increased releases of the dissolved metals to watercourses.

The overall mean concentrations of ammonium and phosphate ions in the snowmelt runoff exceeded MPCs 2.3 and 13.3 times respectively. The discharge of effluents with elevated levels of nutrients (e.g. ammonium and phosphate) can improve the survival and growth of aquatic plant organisms, but can also contribute to the eutrophication of the receiving waters (Bartlett et al. 2012). Long-term observation data indicate that the water in the River Mukhavets is constantly contaminated by phosphate, nitrite and ammonium ions; hence, surface runoff contributes to the total pollution by components of prime concern (Loginov 2009, 2010, 2011, 2012).

The concentrations of most of the tested contaminants vary in a similar way, increasing from snow to snowmelt runoff samples (Tables 1, 2, Figure 2b). It is obvious that these impurities did not originate only from atmospheric precipitation. They became accumulated in the snow layer during its formation and contribute to their excessive outflow in the snowmelt surface runoff.

The concentrations of several HMs exceeded MPC levels. The concentration of Zn exceeded MPC in all the samples of snow and snowmelt runoff, and Cu and Mn concentrations also exceeded MPCs in all the tested runoff samples (the overall mean concentration of Zn in snowmelt runoff exceeded MPC 3.2 times, the overall mean concentrations of Cu and Mn exceeded MPCs 4 and 3.1 times respectively). The small decrease in the mean concentration of Cu and Zn in the runoff compared to snow at site 2 is explained by the fact that we were not able to completely avoid the influence of traffic emissions when sampling the snow, and snowmelt runoff was most probably diluted by effluent from another part of the site with a lower concentration of these metals.

The main sources of HM pollution in Brest are vehicle emissions, abrasion and corrosion of vehicle parts (Mn, Zn and Cr are often used as alloying elements in steel, a lot of vehicle details are plated with Zn, trolleybus contacts with power lines are plated with Zn and Cu) and the

**Table 3.** Total amounts of phosphate and ammonium ions in snowmelt surface runoff (SSR) and River Mukhavets runoff (RR) during the winter period

| Total runoff* [thousands of m$^3$] | | Total amount of phosphate ions [tons] | | | Total amount of ammonium ions [tons] | | |
|---|---|---|---|---|---|---|---|
| RR | SSR | RR | SSR | | RR | SSR | |
| | | | [tons] | [%]** | | [tons] | [%]** |
| 265542 | 3764 | 89.4876 | 10.0883 | 11.27 | 125.1764 | 4.1407 | 3.31 |

*Volchek 2005, TCGP 2012b, Technical Code 45-4.01-57-2012 (02250).
**Percentage of the total amount of pollutants found in the River Mukhavets during the winter period.

corrosion of metal roof covers and gutters, as the city has no big industries that could emit heavy metals.

To evaluate the impact of snowmelt runoff on nutrient pollution in the River Mukhavets, the total amount of phosphate and ammonium ions during the winter period (December 2012–April 2013) was calculated for snowmelt runoff and river runoff in Brest (Table 3). The calculation was done for the overall mean concentrations of these pollutants in the Mukhavets for the last 3 years (Loginov 2012) and the overall mean concentrations in snowmelt runoff obtained in our study. The amounts of phosphate and ammonium ions discharged with snowmelt runoff make up 11.27% and 3.31% respectively of the total amount of these pollutants found in the Mukhavets during winter, showing that surface snowmelt runoff is a significant source of pollution by nitrogen and phosphorus compounds. If we take into account the fact that four towns with populations from 13 to 330 thousand people (Brest) are situated on the Mukhavets, the total pollutant load arising from surface snowmelt runoff from urban areas is even higher and presents a serious environmental threat at not only a regional but also a European scale.

A potential threat arises from the fact that the River Mukhavets is a tributary of the Western Bug, a trans-boundary river of the Baltic Sea catchment area. As the mouth of the Mukhavets is very close to the city, a significant percentage of the pollution released may be involved in trans-boundary transport, thereby contributing to the pollution and eutrophication of the Baltic Sea. Unfortunately, we could not make similar calculations for the other pollutants because of the lack of appropriate river water monitoring data.

## 4. Conclusions

The surface runoff formed during snow melting periods in Brest carries a significant pollutant load that exceeds national regulation levels and can cause long-term environmental effects on watercourses if the runoff is discharged into them without prior treatment. In Brest a significant percentage of the surface runoff is allowed to drain untreated into the River Mukhavets and flows with the river waters into the Western Bug, a trans-boundary river of the Baltic Sea catchment area. Thus, surface runoff from the Brest area can contribute to the trans-boundary transport of elements. The pollutants of primary concern during the winter period are TSS and chloride ions, because their concentrations show the greatest excess compared to MPCs, and phosphate and ammonium ions because of the eutrophication they may cause.

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